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## RELAXATION PROCESSES IN IRRADIATED ZnIn<sub>2</sub>Se<sub>4</sub> MONOCRYSTALS

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**Abstract:** It was determined the nature, parameters of recombination centers from the study of stationary and kinetic characteristics of photoconductivity in different values of radiation intensity and temperature and possible formation mechanism was clarified in ZnIn<sub>2</sub>Se<sub>4</sub> photoresistors grown by gas transportation method.

**Key words:** photoconductivity, relaxation, recombination, electron capture, spectrum, fast centers, temperature, intensity.

### 1. Introduction

A<sup>II</sup>B<sub>2</sub><sup>III</sup>C<sub>4</sub><sup>VI</sup> class crystals, having anisotropic crystalline structure, are of importance as materials for means receiving and storing information [1, 2]. The observation of a number of events, which are different from binary analogies in the condition of complication of content, is related with the compression of crystal lattice on a certain preferred direction in threefold combinations (it is called tetragonal compression) and the presence of two atoms that are not equivalent, as well as vacancy in cation sublattice. The last property and having wide homogeneity area lead to the formation and management of a number of "specific" defects in these materials [1]. Acting as a capture and recombination centers, these defect levels form photosensitivity of materials and time parameters of recombination processes. In the presented work, the determination of energy spectrum, parameters and type of local centers in ZnIn<sub>2</sub>Se<sub>4</sub> crystals and their management capabilities have been carried out by the study of stationary and kinetic characteristics of photoconductivity.

For measuring photoelectric properties, ZnIn<sub>2</sub>Se<sub>4</sub> crystals were obtained by gas transformation method through iodine and have triangular prism form. X-ray structure analysis indicates that, the faces of trihedral prism correspond to (112), (001) and (112) planes. The most grown face (112) is the face, which is illuminated in researches and provided with contacts. The optical arrow of crystal forms 37° angle with this face.

Natural grown face of ZnIn<sub>2</sub>Se<sub>4</sub> photoresistors has sensitivity band, which corresponds to photons with 1.1÷2.3eV energy. Sharply increase of optical absorption with high verticalness corresponds to 1.85 eV at room temperature and shows that ZnIn<sub>2</sub>Se<sub>4</sub> monocrystals are direct band semiconductor. Additive levels are associated with photoconductivity, when  $h\nu < 1.8eV$  at spectral distribution of stationary photoconductivity, but when  $h\nu > 1.8eV$ , it is associated with the photoactive absorption, occurring from subzones of fragmented valence band, in depth of fundamental absorption edge [1]. The energy capacity of additives defined from stationary photoconductivity spectrum is 1.70 and 1.32eV. The dependences of photocurrent on temperature, excitation and time, as well as the formation of photosignal in combined illumination occur with the presence of both additive levels and adhesion centers [3]. These events are associated with the presence of two type local levels, which act as a recombination center in band gap in ZnIn<sub>2</sub>Se<sub>4</sub> crystals. These recombination centers differ for the value of effective cross-section of the capture

of photoelectrons. The centers with the same hole capture cross-section and with weak capacity of free electron capture ( $S_{nr}$ ) are called  $r$ , but with fast capture features are called  $S$  centers ( $S_{nr} < S_{ns}$ ;  $S_{pr} \geq S_{ps}$ ). The determination of set of parameters of local centers and the management of recombination process have been carried out based on kinetics of photoconductivity.

In general, three areas can be differed in the process of photocurrent reduction relaxation in the case of elimination of excitation – time dependence of photocurrent, formed in the illumination of  $ZnIn_2Se_4$  photoresistor at low temperature.

- 1) Decrease of instant ( $t_1 \sim$  within microsecond) photocurrent – fast relaxation
- 2) Decrease with relatively low speed ( $t_2 \cong$  millisecond) – slow relaxation.
- 3) Keeping its value for a long time (for hours) by being  $10^4$  times higher than long-term ( $t_3 \cong$  minute) dark current. It is called residual photocurrent effect (RP).

Such relaxation of photocurrent must be associated with the complexity of recombination scheme and the formation of recombination barriers as a result of non-homogeneous distribution of local centers in its volume in  $ZnIn_2Se_4$  crystals. In general case, the dependence of photocurrent on time can be expressed as  $i = i_0 \exp(-\frac{t}{\tau})$ ,  $\tau$  is characteristic time.  $\tau = 10^2 S$  in the third area. But, after certain period exponentiality is violated, instantaneous value of  $\tau$  increases and becomes  $10^5$  sec. RP depends on spectral composition of exciting light and corresponds to spectral contour of specific photoconductivity.  $\frac{\sigma Q F}{\sigma Q} = 10^4$  – at low temperatures and rapidly decreases in the extinction area of photoconductivity by the increase of temperature. RP disappears at  $T > 280 K$ .

In order to remove RP, either high electric field must be applied to photoresistor or it must be irradiated with IR light with  $\sim 1.0$ -micron wavelength. Extinction spectrum in the last one corresponds to extinction spectrum of photoconductivity, and its maximum corresponds to  $\lambda = 1,2$ -micron, its red boundary to 2-micron.

It should be noted that, strong electric field and IR light only partially extinguish RP. Returning photoresistors to initial state is possible by heating them up to 350 K in small areas. The explanation of RP on the base of current theories is explained by the presence of recombination barriers of  $ZnIn_2Se_4$  crystals for conductivity and macroscopic non-homogeneities in the volume. In order to eliminate these recombination barriers, photoresistor should be irradiated with special light. In this case, the condition for RP does not exist anymore and it becomes possible to define the parameters and nature of centers, managing recombination process.

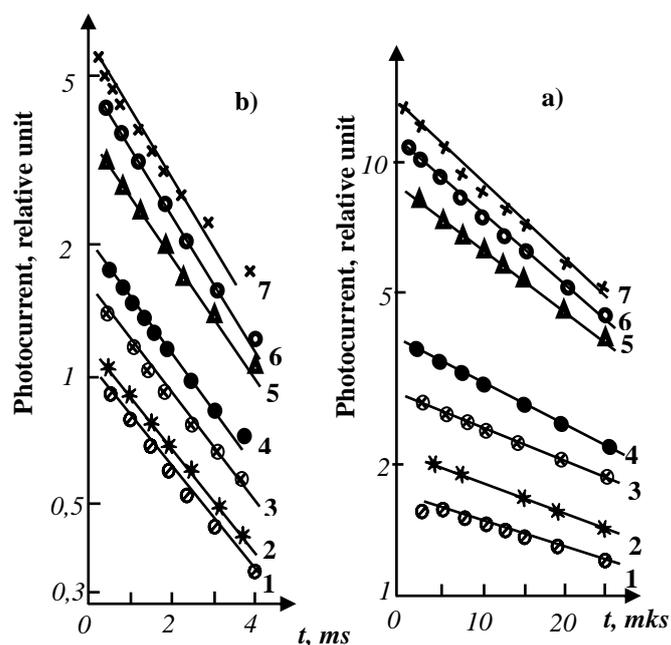


Fig. 1. Relaxation of fast (a) and slow (b) components of photocurrent at different values of exciting effect depending on time in  $ZnIn_2Se_4$

Relaxation curve of photocurrent is complicated in polycentric semiconductors. Duration of relaxation of holes is  $\tau_p \approx 10^{-9} \div 10^{-10}$  sec, electrons is  $\tau_n \approx 10^{-6}$  sec in electron type semiconductors.

If the duration of exciting impulse  $\Delta t$  satisfies  $\tau_{pi} < \Delta t < \tau_{ni}$ , holes are captured by appropriate centers during impulse. And, electron relaxation begins after the end of impulse and defines electron capture characteristics of center. The impulses of ЛГУ-21 gas laser, having  $\Delta t = 10^{-8}$  sec duration, satisfy this condition. It has been used special background lighting in order to eliminate the impact of adhesion level on kinetics of photocurrent. Such condition allows defining the appropriate duration of relaxation ( $\tau_i, i = s, r$ ) by allowing to watch recombination through different centers in  $ZnIn_2Se_4$  photoresistor. Relaxation curve from oscillogram of photocurrent is characterized in two linear areas (fast and slow) in semi-logarithmic scale.

$\tau$  - time period, which is found in the kinetics of photocurrent, has an autonomic meaning in the condition of weak change of filling recombination centers. As unbalanced holes are captured during impulse, the defined relaxation duration belongs to  $S$  and  $r$  centers, properly [4]:

$$\Delta n \approx g_s \exp\left(-\frac{t}{\tau_s}\right) + g_r \exp\left(-\frac{t}{\tau_r}\right)$$

$g_s$  and  $g_r$  define recombination rate of unbalanced electrons through appropriate recombination centers and depend on effective cross-section of electron capture with centers and the filling of them with electrons:  $g_s + g_r = 1$  [3].

The amplitude of slow component defines photosensetiveness of photoresistors and concentrations of these centers relatively depend on the filling of  $r$  and  $s$  centers at the beginning. The observation of fast component is the indicator of the filling of  $r$  and  $S$  centers with holes in the condition of using short impulse. The value of  $\tau_i$  quantity that characterizes the relaxation of photocurrent depends on the illumination intensity, ie the amount of unbalanced carriers, on temperature, ie filling rate of centers fulfilling recombination process and on the nature of ionization. The relaxation of photocurrent decreases with the increase of intensity of relaxation period of both fast and slow recombination channel at different irradiation intensities in  $ZnIn_2Se_4$  photoresistor. Relaxation time is  $10^{-5}$ sec for  $\tau_s$ ,  $10^{-3}$ sec for  $\tau_r$  and it indicates that capture cross-section of the main carriers of appropriate recombination centers sharply differs and recombination process occurs gradually.  $\tau_r^{-1}(\Delta n)$  and  $\tau_s^{-1}(\Delta n)$  dependences are linear for  $ZnIn_2Se_4$  and on the base of photoconductivity theory, this defines the capture coefficients of electrons by  $r$  and  $S$  centers

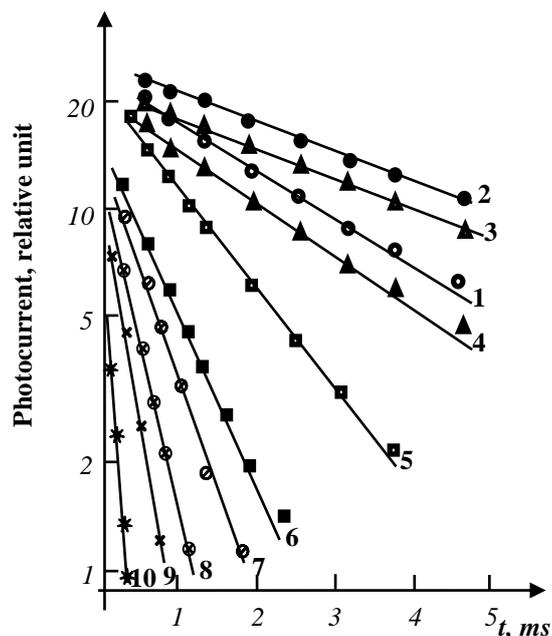


Fig. 2. Relaxation curves of photocurrent at different values of temperature in  $ZnIn_2Se_4$  crystals.

1 – 77 K; 2 – 100 K; 3 – 110 K; 4 – 121 K; 5 – 131 K; 6 – 145 K; 7 – 155 K; 8 – 170 K; 9 – 200 K; 10 – 240 K.

and  $S_{nr}$  and  $S_{ns}$  quantities which are called effective cross-section of capture ( $S_{nr} = (2 \div 4) \cdot 10^{-13} \text{ cm}^2$ ,  $S_{ns} = 3 \cdot 10^{-17} \text{ cm}^2$ ). Capture cross-section of holes by slow recombination centers is determined according to the value of ratio of  $S_{nr}/S_{pr}$  defined from stationary characteristic and corresponds to ( $S_{pr} \sim 10^{-15} \text{ cm}^2$ ). The comparison of value of capture cross-section with approximate value of cross-section of atom ( $10^{-16} \text{ cm}^2$ ) indicates the capture of holes in Coulomb attraction field, and the capture of electrons by neutral centers, ie local levels acting as a recombination center is acceptor with one charge in  $\text{ZnIn}_2\text{Se}_4$  photocrystals. The relaxation of slow component of photoconductivity at different temperatures complies with thermal extinction of photoconductivity. The decrease of  $\tau_r$  by the increase of temperature is related with the increase of possibility of exchange of holes between slow  $r$  centers and valence band.

The analysis of experimental results shows that,  $r$  centers, managing photosensitivity in  $\text{ZnIn}_2\text{Se}_4$  monocrystals, are associated with  $\text{Zn}_{In}$  type levels, which are called “antistructure defects” and occur in the exchange of III group ion with II group ion in cation sublattice and, as well as with  $[V_{Zn}:J_{Se}]$  type complexes, which are formed in the replacement of chalcogen with transagent. And, donor type local levels, distorted kinetics of photocurrent by forming adhesion centers as  $\text{In}_{Zn}$  and  $V_{Se}$

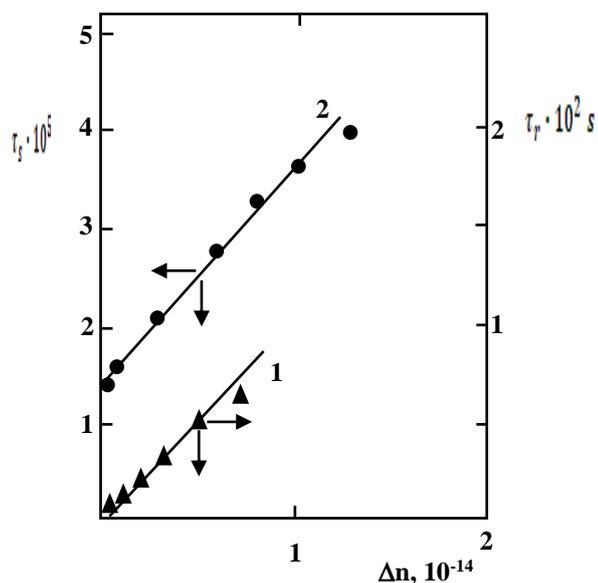


Fig. 3. Dependence of inverse value of relaxation time on concentrations of unbalanced carriers in  $\text{ZnIn}_2\text{Se}_4$  crystals. 1 –  $r$  centers; 2 –  $s$  centers

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## ПРОЦЕССЫ РЕЛАКСАЦИИ В ОБЛУЧЕННЫХ МОНОКРИСТАЛЛАХ $\text{ZnIn}_2\text{Se}_4$

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**Резюме:** Методами исследования стационарных и кинетических характеристик фотопроводимости в выращенных методом газотранспортной реакцией монокристаллах  $\text{ZnIn}_2\text{Se}_4$  при различных температурах и интенсивности освещения было определено природа и физические параметры рекомбинационных центров, их возможные механизмы возникновения.

**Ключевые слова:** фотопроводимость, релаксация, рекомбинация, электронный захват, захват дырок, спектр, быстрые центры, температура, интенсивность

## ŞÜALANMIŞ $ZnIn_2Se_4$ MONOKRİSTALLARINDA RELAKSASIYA PROSESLƏRİ

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**Xülasə:** Qazdaşınma üsulu ilə göyərdilən  $ZnIn_2Se_4$  fotorezistirlərində fotokeçiriciliyin stasionar və kinetik xarakteristikalarının şüalanma intensivliyinin və temperaturun müxtəlif qiymətlərində tədqiqindən rekombinasiya mərkəzlərinin təbiəti, parametrləri təyin olunmuş, mümkün yaranma mexanizmi aydınlaşdırılmışdır.

**Açar sözlər:** fotokeçiricilik, relaksasiya, rekombinasiya, elektron zəbti, spektr, cəld mərkəzlər, temperatur, intensivlik